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Photoluminescence from Bulk GaN Substrates

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Photoluminescence from bulk GaN substrates

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics / Applied Physics at Virginia Commonwealth University.

By

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Abstract

By Marrwa Abdullah Alrrshedan

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Virginia Commonwealth University. Virginia Commonwealth University, 2012

Major Director: Michael A. Reshchikov, Associate Professor, Department of Physics

Photoluminescence (PL) has been studied from different types of bulk GaN samples grown by hydride vapor phase epitaxy technique at Kyma Technologies. Point defects in bulk and at the surface affect the electrical and optical properties of GaN and could be analyzed by PL. The surface of the samples was polished with different techniques: one is chemical mechanical polish (CMP) and another is mechanical polish (MP). PL data from MP and CMP surfaces show that PL intensity from the CMP-treated surface is much higher than that from the MP-treated surface. This can be explained by defects formed during the process of MP polish. However, after the MP-treated surface is etched with RIE method, the optical quality of the MP-treated surface improves. In particular, as the depth of etching increases from 50 nm to 700 nm, the PL intensity increases by a factor of 1000. PL from the CMP surfaces of undoped bulk GaN samples contains a broad red luminescence (RL) band and a broad green luminescence (GL) band. However, PL from the CMP surfaces of Fe-doped GaN samples contained a blue luminescence band (labeled as BL2 in literature) and the yellow luminescence (YL) band. PL from MP-treated surfaces (both undoped and Fe-doped) was very weak and it contained

relatively narrow red and green bands. These bands, labeled RL2 and GL2, respectively, are quenched at relatively low temperatures, in contrast to the RL and GL bands which are almost independent of temperature in the range from 15 to 300 K.

Chapter 1: Introduction

1.1 Motivation

The next important semiconductor material after silicon is gallium nitride (GaN). It is direct and wide bandgap semiconductor of (3.4 eV at room temperature). It has special properties to operate at higher temperature, higher power density, higher voltage and higher frequency that make it very exciting to use in future electronic systems. It is an ideal material to emit light and is used to fabricate blue and violet light emitting diodes (LED) as well as laser diodes (LD).^{1,2} GaN contains many structural and point defects where these defects greatly affect the electrical and optical properties of the host material. In this work, we study free-standing bulk GaN templates and investigate the properties of defects in bulk GaN.

Point defects are defects of crystal lattice of atomic size. They are common, especially vacancies, when atoms randomly change their places at high temperatures of growth, leaving empty lattice sites. Defects play an important role in the optical and electrical properties of semiconductors.^{5,6} Point defects in bulk GaN samples grown by hydride vapor phase epitaxy (HVPE) affect the behavior of these samples.

Photoluminescence (PL) can be used as a tool to study the properties of defects in bulk GaN. PL is the emission of photons from a material produced by light from an excitation source. The process of PL starts when a material is illuminated with above-bandgap light. The photons are absorbed by the material, then the material emits its own photons with lower energy. The band structure of GaN has a wide gap (3.4 eV at

room temperature) between the valence and conduction bands. The PL is an important tool in the characterization of defects due to its unique sensitivity to discrete electronic states.

Figure 1.1 shows schematically how the PL is excited by a laser. The surface of GaN is illuminated with light which has a photon energy above the bandgap energy. Electrons in the valence band are excited to the conduction band. After the electron is excited to the conduction band, it leaves a hole in the valence band. The hole dissipates the energy and moves toward the top of the valence band. The electron in the conduction band also dissipates the excess energy in the form of phonons and moves to the bottom of the conduction band. As the hole freely moves in the valence band, an acceptor with a level in the gap may attract and capture the hole: then the hole becomes a bound hole. Eventually, the bound hole and a free electron from the conduction band can recombine.⁶ There are two different ways how the energy from the electron-hole recombination is released: via emission of phonons and photons. The emission of photons is called photoluminescence. The phonons dissipate the remainder of energy.

Although, the progress is being made in the understanding of bulk and surface defects in GaN, bulk GaN substrates are still a big issue and point defects in these substrates are not well understood. One of the most common techniques that have been used to study defects in various semiconductors, including GaN, is PL. In this thesis, bulk GaN substrates were grown by hydride vapor phase epitaxy (HVPE) and were studied through the use of photoluminescence.

Chapter 1 Figures

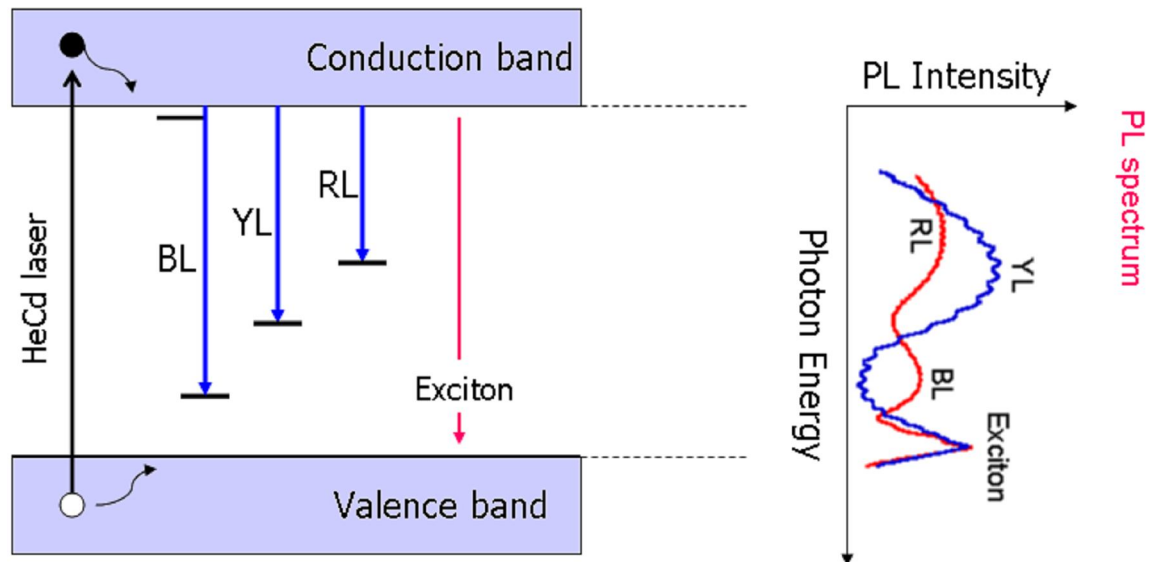


Fig. 1-1: Band diagram for a semiconductor with main electron transitions (on the left) and PL spectrum (on the right) illustrating the origin of the PL bands.

Chapter 2: Literature review

2.1 Introduction

GaN semiconductor is one of the most attractive semiconductor materials. In 1969, Maruska and Tietjen succeeded in growing single crystalline GaN on sapphire substrate by Hydride Vapor Phase Epitaxy (HVPE).⁹ They have also established that GaN has bandgap energy of about 3.39 eV at room temperature, and that GaN could be grown with a high purity to be used in electrical and optical devices.⁹ In 1970's, Pankov et al.¹⁰ and Maruska et al.¹¹ declared the first metal-insulator-semiconductor (MIS) type blue – green light emitting diode (LED) based on GaN. The producing of a single crystalline GaN by Molecular Beam Epitaxy (MBE) was successfully achieved in 1974 by Akasaki and Hayashi.¹² The first practical MIS type blue-green LED based on GaN grown by HVPE was reported in 1981.¹³

Although the development of growth of free-standing GaN by HVPE technique has been going on for several years, the quality of this material is generally still not high enough and the cost is not low enough for large scale production. In 1998, Porowski et al.¹⁴ have succeeded in synthesis of GaN bulk crystals under high pressure (15-20 Kbar) and high temperature (1400-1600°C). This material was reported to be practically free of extended defects. In the same time, Usui et al.¹⁵ have succeeded in growth of a few tens of a micron thick GaN on a 2” diameter sapphire substrate by using HVPE. However, it cannot give any fundamental advantages of homoepitaxy since the GaN is still on a sapphire substrate. One year later, Kim et al.⁴ reported on the preparation and properties

of free-standing GaN substrate with a 350 μm thickness and 10 mm \times 10 mm area prepared by the HVPE growth technique. The PL spectrum was measured in their work at 10 K and at room temperature. They found that the PL spectrum for the free-standing GaN substrate measured at 10 K (as shown in Fig. 2.1) consists of the excitonic emission and the deep donor-acceptor pair (DAP) recombination at 1.8 and 2.2 eV. However, there was no emission from the shallow DAP recombination. Fig. 2.2 shows the PL spectrum at room temperature for a free-standing GaN substrate. It consists of the weak emission at 3.4 eV from the bandedge recombination and at 2.2 eV which is the yellow emission band.⁴ This work concluded that the free-standing GaN substrate has been found to be optically and electrically of high quality but still needs to be improved in crystal quality.

As the HVPE method improved, the quality of thick GaN layers is also paved the way for investigating extended defects with more confidence. In 2002, Liliental-Weber et al.¹⁶ showed that the dislocation density drastically decreases with increasing thickness of GaN. In 2001, Samsung Advanced Institute of Technology (SAIT) in Korea has produced free-standing GaN templates grown by HVPE which have the superior quality to date, combining the highest bulk mobility of electrons, very low density of dislocations, and the lowest concentration of uncontrolled donors and accepters.⁶ In 2001 and 2002, Reshchikov et al.⁶ measured PL spectrum from free-standing GaN produced by SAIT at 15 K and at room temperature. They found that PL spectrum at low temperature contains multiple exciton peaks above 3.3 eV. The ultraviolet luminescence (UVL) band at 3.26 eV and a broad yellow-green band (with a maximum at 2.2-2.4 eV) were also studied. A very weak blue luminescence (BL) band at 2.9 eV and the RL band

at about 1.8 eV could be also resolved. The PL bands, except for the RL band and the yellow green band, are thermally quenched at room temperature. However, the broad yellow-green band and the near-bandedge emission peaking at about 3.41eV could be observed at room temperature, see Fig. 2.3. The result of their study is that the YL and GL bands, that are present in a high-purity GaN free-standing template grown by HVPE, are related to the same defect, namely to the gallium vacancy-oxygen complex.

The growth process of HVPE to produce high-quality thick ($\geq 300\mu\text{m}$) GaN layer on sapphire and the removal of such a layer from the sapphire substrate to obtain free-standing GaN material were described by Monemar et al.¹⁷ In this work, it was discussed that defects like dislocations, micro-cracks and pits were produced during growth. The laser lift-off technique is shown to be practical technology for producing free standing GaN material at about 700°C. This work described problems which are related to the growth process and how this problem affects the quality of thick HVPE GaN wafer. The main problem of free-standing material is large bowing of such a wafer, because of the stress at the former GaN – sapphire interface.

2.2 Growth of GaN samples

Hydride Vapor Phase Epitaxy (HVPE) is the most common technique to grow bulk GaN material, due to high growth rate, a comparatively simple growth chemistry and economic gas consumption as compared to other vapor phase growth techniques. HVPE has proven to be an effective technique to fabricate free-standing GaN substrates.¹⁸ In the

case of producing high-quality thick ($\geq 300 \text{ }\mu\text{m}$) GaN layers, the high growth temperatures ($> 1000^\circ\text{C}$) were used. The thick GaN layers were grown initially directly on the sapphire substrate. These thick layers were then removed from the sapphire substrate (Fig 2.4). A successful technique for separation of thick GaN layers from their sapphire substrate is a laser lift-off (LLO). Fig. 2.5 shows a simple system for the LLO. The laser is used to melt GaN near the GaN/sapphire interface. It has a wavelength of about 353 nm to be absorbed in GaN. The 2" GaN wafer (on sapphire) is placed upside down over a small volume heated with a hot plate arrangement to about 700°C .¹⁷ The GaN layer is essentially strain-free at this temperature. The whole sample holder is linked to an x-y stage which is moved in controlled fashion via a computer.

The laser spot is moved from the perimeter to the center of the wafer in a spiral style. The spot size is less than 1mm in diameter. A thin GaN layer (a few tenths of nm) within the laser absorption length decomposes into liquid Ga and N_2 gas since the laser spot heats the GaN at interface with the sapphire. LLO is a useful technique for the removal of the substrate from these thick wafers, without cracking of the wafer. Free-standing GaN wafers produced via LLO have main problem which is the large bowing of the wafers. When the GaN layer is residing on the sapphire, it has a convex bowing from the thermal mismatch during cool down. The size of this bowing is large: up to $500\mu\text{m}$ over a 2" wafer.¹⁷ The concave bowing becomes smaller after lift-off the layer has relaxed but still several hundreds of μm in the center of a 2" wafer as shown in Fig. 2.6.

2.3. Luminescence Related to Point defects in undoped GaN

Fig. 2.7 shows the positions of the energy levels calculated for the doped and undoped GaN.¹⁹ These levels can be compared with the positions of PL peaks determined from the luminescence studies. We will focus in photoluminescence (PL) spectrum measured from undoped GaN layers. The PL spectrum from undoped GaN usually contains a broad yellow luminescence (YL) band at about 2.2 eV, and it is still not clear what kind of defects contribute to the broad YL band (Fig. 2.8). In undoped GaN grown by HVPE method, the YL is replaced by a green luminescence (GL) band with a maximum at about 2.4 eV.⁶ This GL band is attributed to another charge state of the defect responsible for the YL band. Sometimes, a red luminescence (RL) band is observed at about 1.8 eV, see Fig. 2.8. In the free-standing GaN template, the RL band could be seen as a shoulder to the YL band. Another luminescence band that could be discovered in undoped GaN is the blue luminescence (BL) band at about 2.9 eV which is related to a different defect.

Chapter 2 Figures

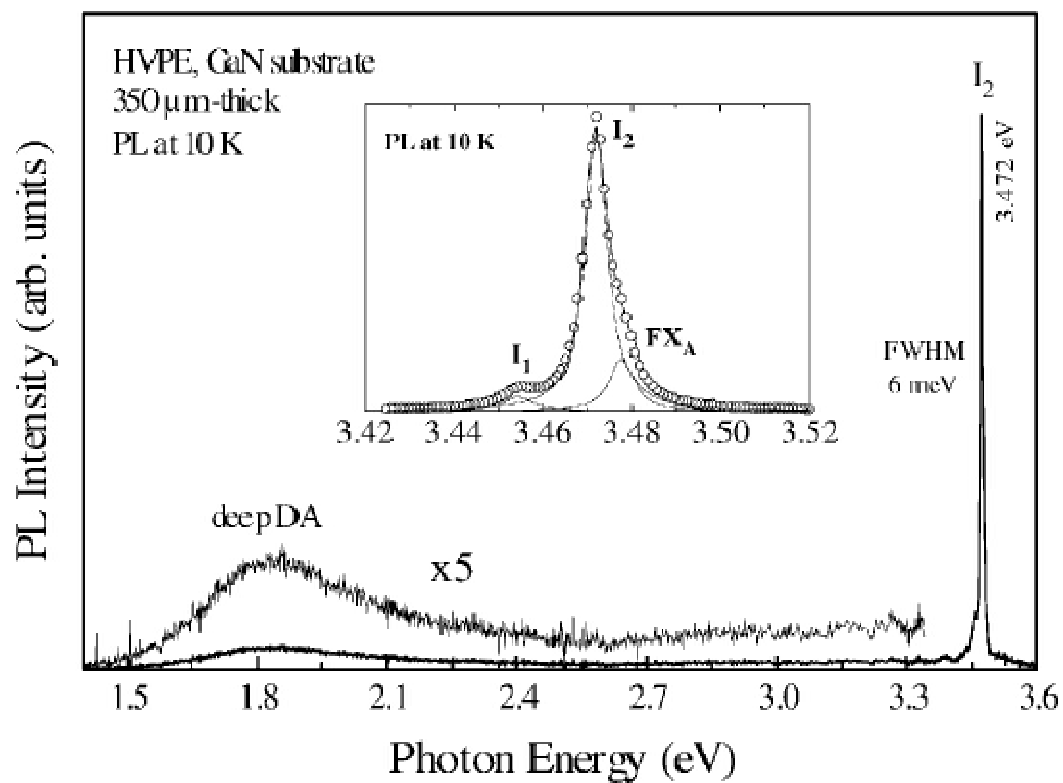


Fig. 2.1: PL spectrum measured at 10 K for bulk GaN substrate (Ref. 4).

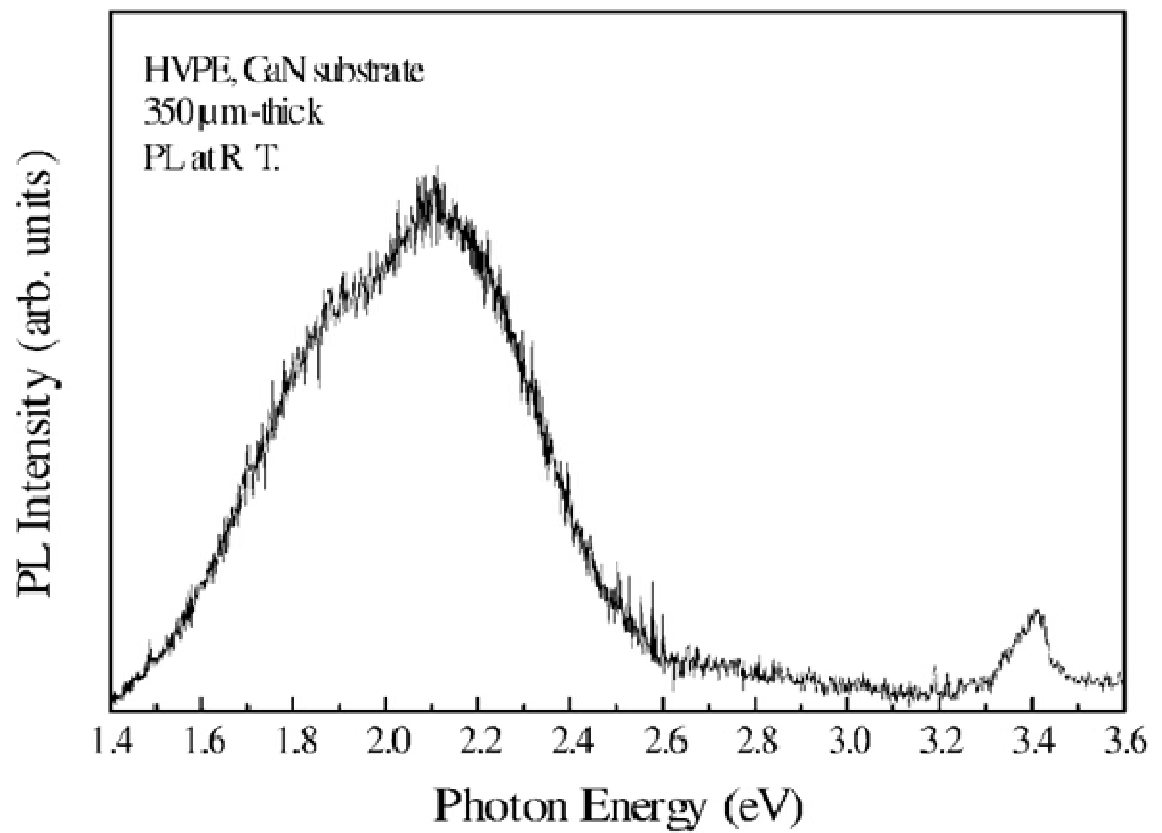


Fig. 2.2: PL spectrum measured at room temperature for bulk GaN substrate (Ref. 4).

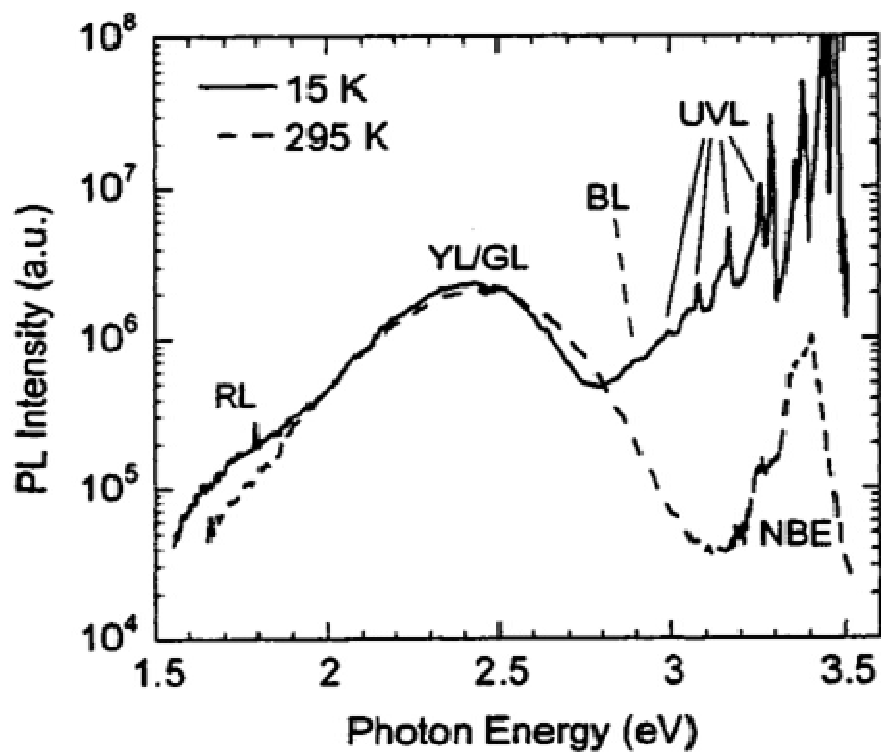


Fig. 2.3: PL spectra from a freestanding GaN template at 15 and 295 K. Exciton part at 15 K is cut in order to present better the defect-related bands (Ref. 6).

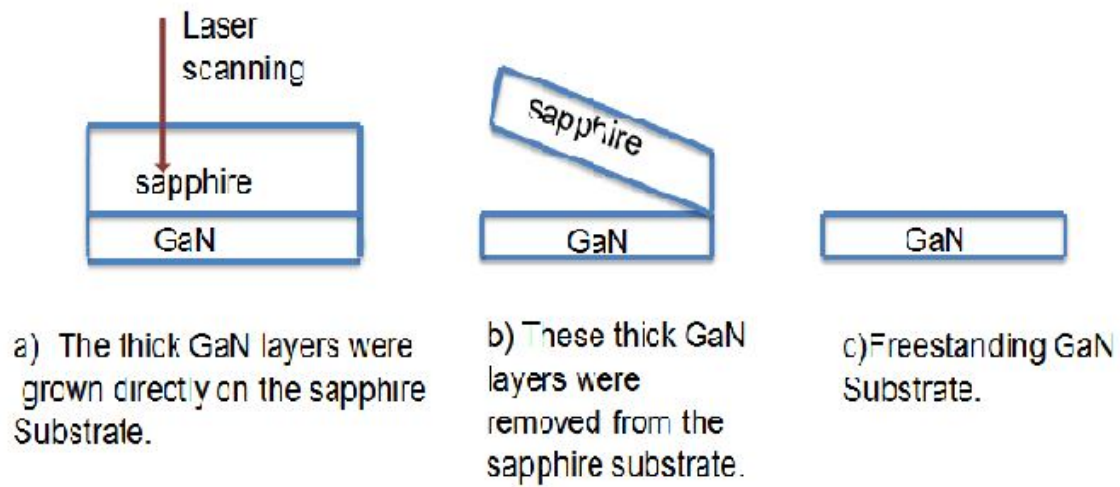


Fig 2.4: Preparation of bulk GaN sample by HVPE and LLO techniques.

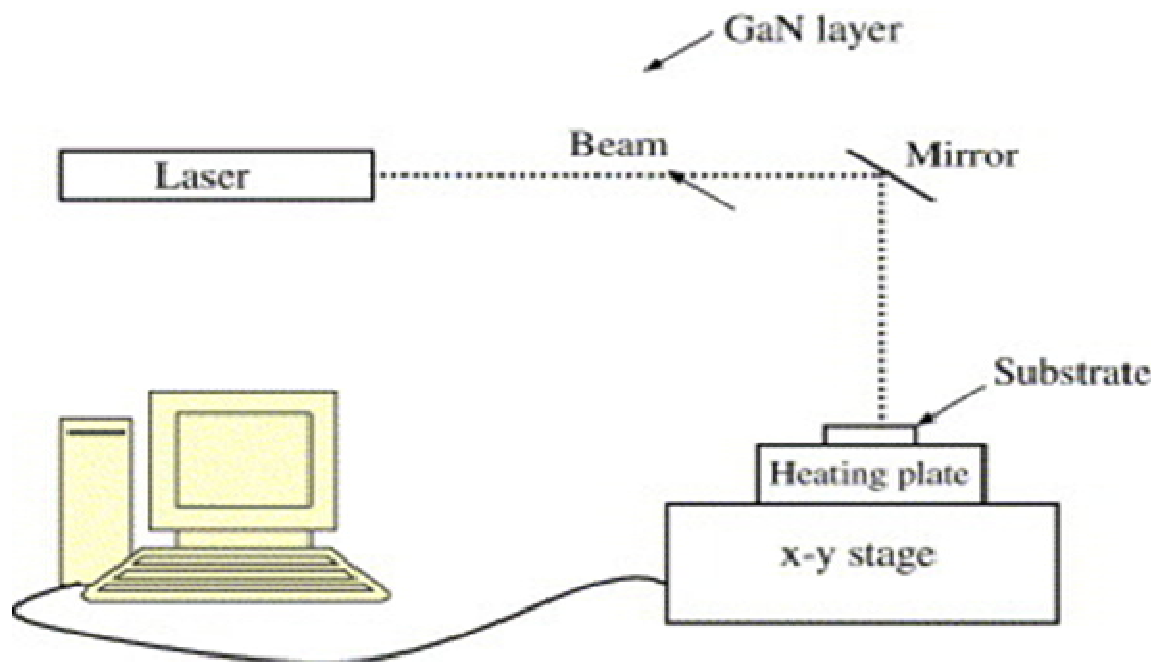


Fig. 2.5: Schematic picture of the laser lift-off set-up, using a computer controlled x-y stage where the hot plate with the wafer is placed (Ref. 17).

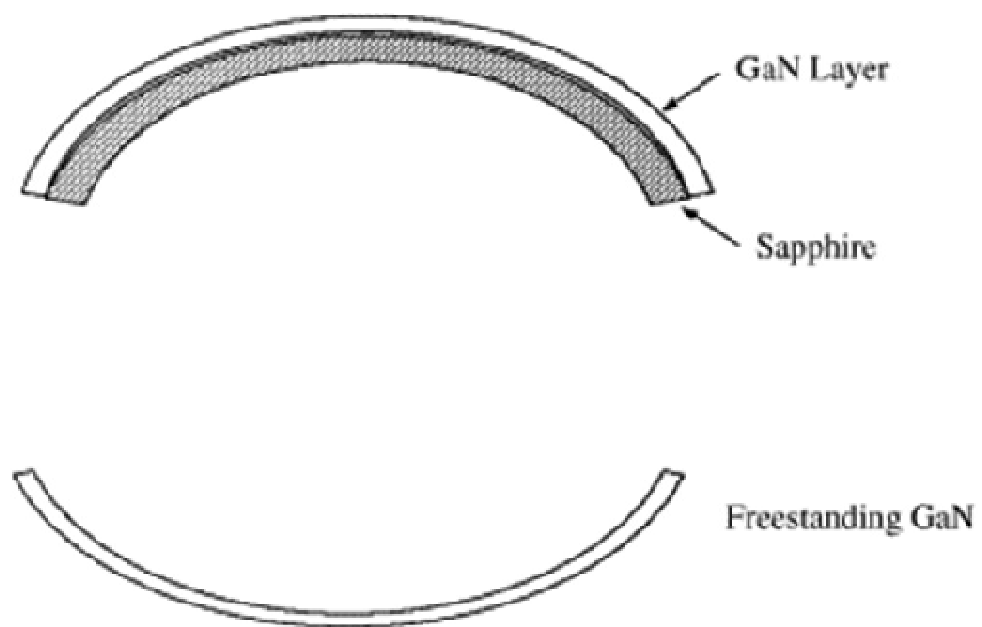


Fig. 2.6: Schematic illustration of the bowing of a thick GaN wafer on sapphire before and after lift-off (Ref. 17).

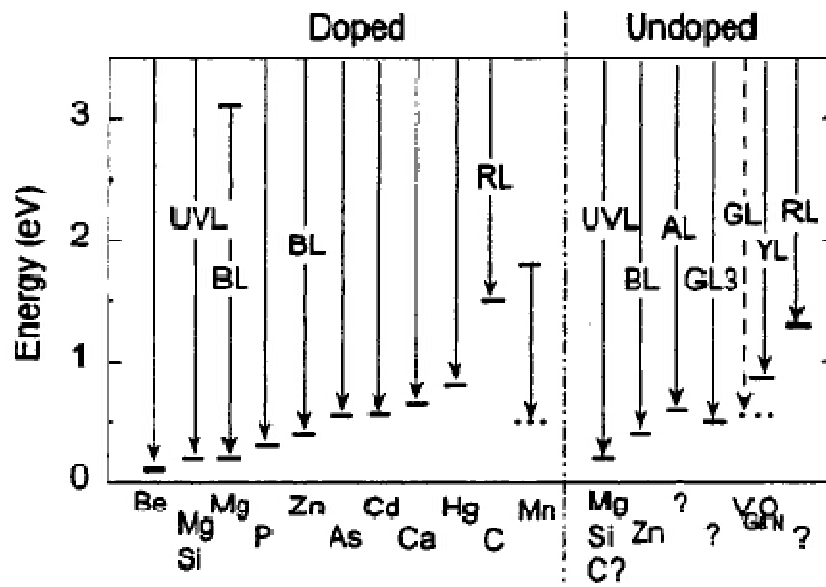


Fig. 2.7: Radiative transitions associated with major doping impurities and unintentionally introduced defects in GaN. For the $V_{Ga}O_N$ complex, two charge states are shown (YL and GL bands) (Ref 6).

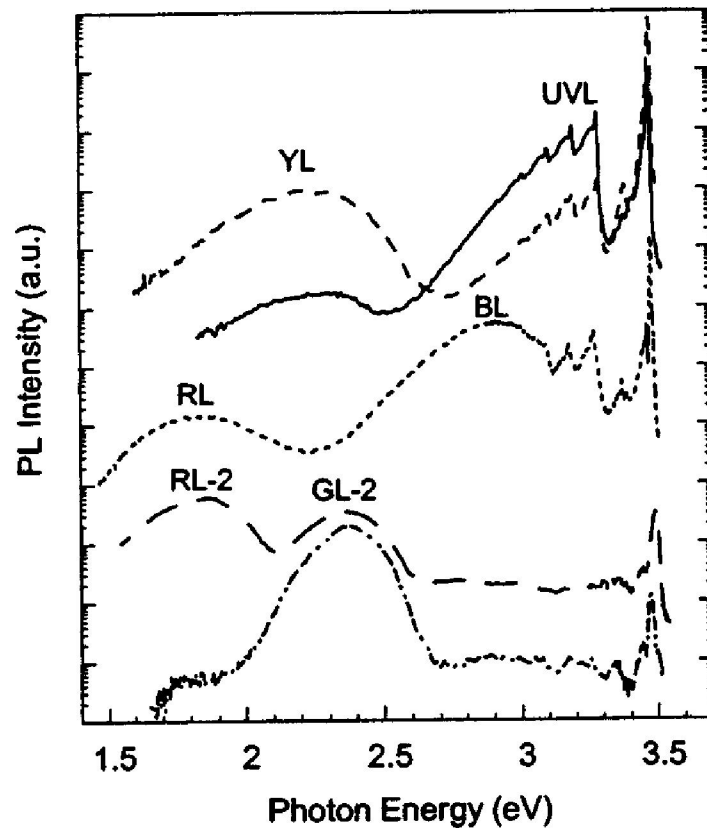


Fig. 2.8: PL spectra from undoped GaN samples at 15 K (Ref 6).

Chapter 3: Experiment

3.1 Experimental setup

In order to measure photoluminescence of semiconductors, the following components are usually included in a setup:

1. Light source (HeCd Laser)
2. A lens to focus light on the sample
3. A cryostat with a sample holder and windows
4. Collection optics
5. Monochromator with moveable grating and two variables slits (entrance and exit).
6. Detector (photomultiplier tube)
7. Electronics to analyze the signal

The photoluminescence experimental setup is shown in Fig 3.1. In this setup we are using a HeCd laser (model IK3552R-G) from Kimmon Electric Company with a total power of 50 mV, emitting at the wavelength of 325 nm. The laser is used as an excitation source for PL, and it produces photons with energy of 3.81 eV (UV region of the spectrum). The laser beam is directed through a set of neutral-density filters (NDF) to the sample, which is mounted to a sample holder inside an optical cryostat. The closed cycle cryostat from Janis Research Co. (model DE-202FF) allows changing temperature in the range from 15 K to 320 K. After the PL is emitted from the sample in all directions, part

of the PL is collected with a lens called a condenser and placed at its focal distance from the sample, so that a parallel beam of emission passes through a dark tube until it reaches another concave lens that focuses the emission onto a slit of a monochromator. A color glass filter is placed before the monochromator to cut parasitic emission with energy lower than 3.5 eV, which is reflection of the laser light from the sample surface in direction of the first collecting lens. Two slits (at the entrance and exit of the monochromator) reduce the range of wavelengths selected by the monochromator, where the smaller slit width provides the better resolution. However, the intensity of the signal decreases proportionally to the square of the slit width (if the widths of two slits are kept equal). The width of each slit could be varied from 0.002 to 1mm. There is a grating inside the monochromator, which disperses the emission in order to obtain a PL spectrum. The purpose of the grating is that only one wavelength of light can exit the monochromator at a time. Different wavelengths can be obtained by rotating the grating. The PL emission, after exiting the monochromator, is detected by a photomultiplier tube (PMT). The PMT is cooled to about 230 K to reduce electrical noise.

3.2 Description of the samples studied in this work

To study the PL from freestanding GaN substrates, four different samples from Kyma²⁰ were used in this work. These included two semi-insulating samples doped with Iron (Fe) and two undoped n-type samples. The main parameters of the samples are given in Table 3.1.²⁰ All the samples were grown on c-plane sapphire substrate with HVPE method which grows a thick layer of GaN substrate (more than 400 μm -thick) on

sapphire, then the sapphire was removed by LLO technique as described in Chapter 2. After removal of the sapphire, the layer of GaN is cut to the size of 10×10 mm for all samples. Finally, both sides were polished with Chemical Mechanical Polish (CMP) or Mechanical Polish (MP). Since GaN was grown in c-direction, every sample has Ga face and N face, where some surfaces are polished with CMP and others with MP methods (see the description of samples in Table 3.2).

One of the semi-insulating bulk GaN (sample AE 857.14 in Kyma's notation and 857-14 in our notation) has pits on the surface which are shown in Fig 3.2. This sample has Ga-face treated with CMP and N-face treated with MP (Table 3.2). Ga-face of this sample has two characteristic areas as schematically shown in Fig 3.3, where A indicates the pits and B indicates the remaining surface of the sample (background). The MP-treated surface of an undoped bulk GaN (sample AG 1412.4 in Kyma's notation and 1412-4 in our notation) was etched with Reactive-ion etching (RIE) method. It is an etching technology used in microfabrication. It uses chemically reactive plasma to remove material from the surface. The plasma is generated under low pressure vacuum by an electromagnetic field. The etching process was done for the MP-treated Ga-face with SiCl_4 chemical material. The surface of this face was divided into four quarters as shown in Fig. 3.4 where one of the quarters was kept as a control (not etched) area and the three remaining quarters were etched to a different depth. One quarter was etched to the depth of 700 nm, another one – to the depth of 200 nm, and the last one – to the depth of 50 nm.

Chapter 3 Figures

Table 3.1: Properties of bulk GaN samples grown at Kyma ²⁰

Dislocation Density	$10^4 - 10^6 / \text{cm}^2$
Thermal Conductivity	2.5 W/cm-k
Size	10×10 mm
Growth Method	HVPE

Table 3.2: Characteristics of bulk GaN sample in this study

Sample	Type	Doping	Thickness (μm)	Description
1305.3	n-type	undoped	424	CMP of Ga-face and CMP of N-face
1412.4	n-type	undoped	393	CMP of N-face and MP of Ga-face
1412.3	n-type	undoped		CMP of Ga-face and MP of N-face
857.3	Semi- Insulating	Fe	434	CMP of N-face and MP of Ga-face
857.14	Semi- Insulating	Fe	435	CMP of Ga-face and MP of N-face

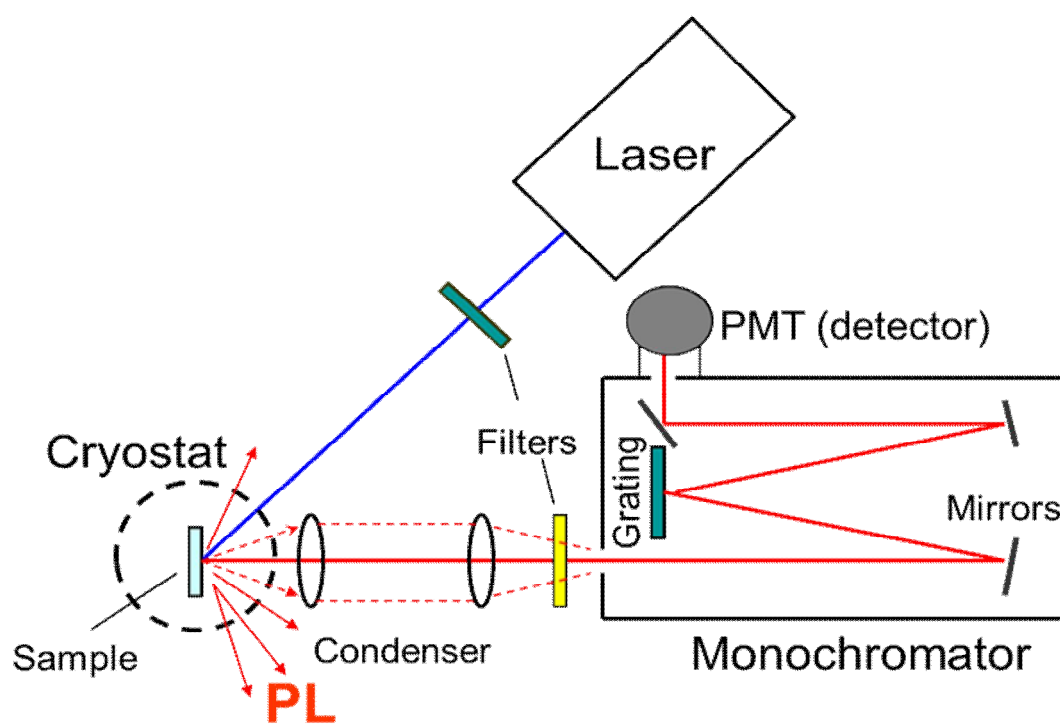


Fig. 3.1: Experimental setup for PL measurements

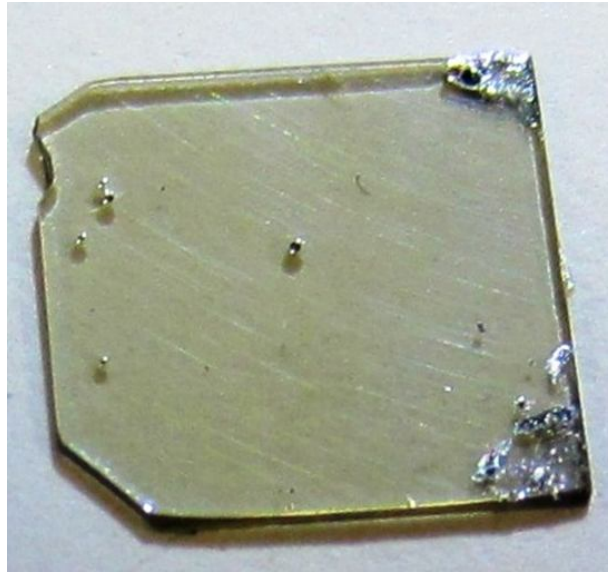


Fig. 3.2: Pits on the Ga-face treated with CMP. Bulk GaN sample (857-14). Large Indium contacts in two corners were used for the Kelvin Probe measurements.

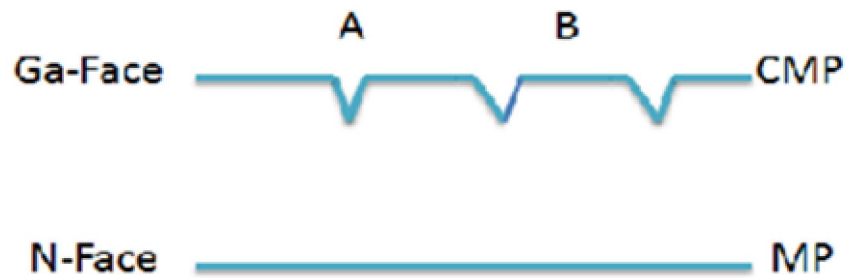


Fig. 3.3: Schematic profiles of GaN samples near the surface.

A: pits on the Ga-face, B: the background.

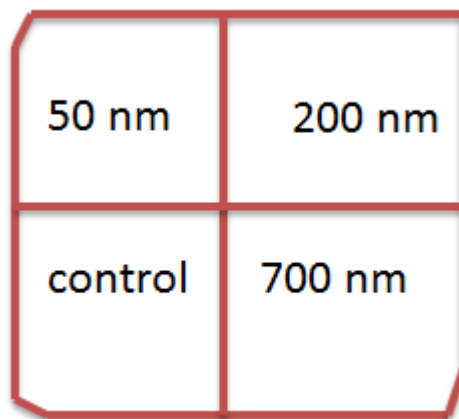


Fig. 3.4: Schematics of the MP-treated Ga-face of undoped GaN sample (1412-4) etched to different depths by RIE with SiCl_4 .

Chapter 4: Experimental Results and Discussion

4.1 Photoluminescence from high-quality undoped GaN (sample 1305.3)

4.1.1 Comparison of PL from Ga and N faces at room temperature

Figure 4.1 shows PL spectra from Ga and N faces for high-quality GaN (sample 1305-3) at 300 K and excitation intensity of 0.3 W/cm^2 . Both faces of the sample were chemically mechanically polished (CMP). The PL spectra from two faces look similar in having a strong PL intensity and the exciton peak at about 3.41 eV. However, there are some differences between them. The major difference is that PL from Ga-face is more intense than that from the N-face. A broad RL band (at about 1.8eV) and GL band (at about 2.4) were observed from N-face, while PL from Ga-face shows just a broad GL band. Generally, PL intensity is high for both faces due to the CMP treatment of the surface.

4.1.2 Comparison of PL from Ga and N faces at low temperature

The PL spectra from Ga and N faces at low temperature for high-quality bulk GaN are shown in Fig. 4.2. The excitation intensity is 0.3 W/cm^2 and the temperature is 15 K. The PL from both faces is strong and the PL spectrum includes the same broad RL band (with a maximum at about 1.82 eV) and GL band (at about 2.4 eV). Both faces also have an exciton peak at 3.46 eV which is close to the bandgap of GaN. It is expected that in high-quality GaN the excitonic PL has the highest intensity at this energy. The main difference between the two faces is that the exciton peak in N-face is wider and has lower intensity

than the exciton peak in Ga-face. Intensity of the defect related PL bands (RL and GL) is also much higher for the Ga face.

4.1.3 Temperature dependence of PL

PL spectra for Ga- and N faces measured at various temperatures are shown in Figs. 4.3 and 4.4, respectively. In both cases, the exciton emission intensity decreases significantly with increasing temperature from 15 to 300 K. The GL band intensity decreases a little for Ga face only. The RL band intensity remained nearly constant in this temperature range.

4.1.4 Dependence of PL on excitation intensity for Ga-face

The dependence of PL spectra on excitation intensity is shown in Fig. 4.5. In this figure, the PL intensity is divided on the excitation intensity. PL intensity of the exciton band has a linear increase with the excitation intensity. The GL band intensity increases faster than linearly with increasing excitation intensity (an increase in Fig. 4.5 corresponds to a super linear increase of PL intensity with excitation intensity), while the RL band demonstrates the opposite behavior (its decrease in Fig. 4.5 corresponds to a sub linear increase with excitation intensity).

4.2 Photoluminescence from CMP- and MP-treated surfaces of undoped GaN (sample 1412.4)

One GaN wafer, after separation from sapphire, was cut into 10×10 mm pieces and its faces polished by MP and CMP. Sample 1412.4 has CMP-treated N face and MP-treated Ga face. Figure 4.6 shows PL spectra from Ga and N faces at 15 K and excitation intensity of 0.3 W/cm². The PL spectrum from CMP-treated N-face has higher PL intensity than that from the MP-treated Ga-face. A broad RL band (at about 1.8 eV) and GL band (at about 2.3) were observed from N-face, while PL from Ga-face contains of RL2 band (at about 1.88 eV) and GL2 (at about 2.38). These peaks will be discussed in more details in the next section. The exciton peak from N-face is much higher than that in Ga-face. The lower intensity of the MP- treated surface is due to the defects at the surface and interface formed during the growth process of the sample.

4.3 Photoluminescence from Fe –doped GaN (samples 857.3 and AE857.14)

4.3.1 Comparison of PL from Ga and N faces at low temperature

As-received semi-insulating bulk GaN (sample 857-3) has Ga-face and N-faces, where the Ga-face is polished with MP and the N-face is polished with CMP, as described in Chapter 3. To compare PL spectra from the two faces, we measured PL spectra at low temperature (15K) and at excitation intensity of 0.3 W/cm² (Fig. 4.7). We observed very weak PL intensity from MP-treated Ga-face. PL spectrum from Ga-face consists of two bands which are named the RL2 band (at about 1.9 eV) and GL2 band (at

about 2.4 eV) because they are identical to the red and green bands reported in Ref 6. The exciton band is very weak and it peaks at about 3.45 eV.

However, PL from N-face, which was prepared by the CMP treatment (Fig. 4.7), is much stronger than that from the Ga-face. Instead of the RL2 and GL2 bands seen in Ga-face, PL spectrum from the N-face shows one broad band (peaking at about 2.2 eV) which is identified as the Yellow luminescence (YL) band. Also, there is an exciton peak (at about 3.46 eV), and it is much stronger than the Ga-face's exciton peak. As we can see, CMP-treated surface gives PL intensity much stronger than the MP-treated surface.

4.3.2 Comparison of PL from Ga-face with and without the 325 nm pass filter

The PL spectra with using the 325 nm filter and without it from the Ga face of the semi-insulating bulk GaN (sample 857.3) are shown in Fig. 4.8. The temperature during the measurement was fixed at 15 K, and the excitation intensity at 0.3 W/cm^2 . Without using the filter, PL spectrum includes artificial lines from laser that are reflected from the sample and enter our monochromator. However, after we use the filter that passes only 325 nm line from the HeCd laser, all artificial lines disappear. Therefore, a filter must be used to cut the parasitic lines.

4.3.3 Temperature dependence of PL from MP-treated surface

The effect of temperature on PL spectrum from Ga-face of sample 857-3 which was polished with MP is shown in Fig. 4.9 where the excitation intensity is 0.3 W/cm^2 . Unfocused laser was used in this experiment to observe the change of RL and GL bands

with increasing temperature. The measurement starts at low temperature (about 15 K) and then increases up to room temperature (300K).

PL spectrum at 15 K contains an exciton peak at 3.47 eV and another relatively sharp peak at 3.3 eV. From the literature, the peak at about 1.8 eV is known as the RL2 band and the peak at about 2.4 eV is known as the GL2 band as illustrated in Fig. 4.9. In general, as the temperature increases, PL intensity decreases. All the bands in this sample are quenched at temperatures above 100 K and disappear at room temperature. The 3.3 eV band decreases similar to the exciton band. Therefore, the results of temperature dependence allow us to conclude that the 3.3 eV band has the exciton nature. Most probably, this PL band is related to an exciton bound to some structural defects. The RL2 and GL2 bands are related to unknown defects.

An interesting result is that the PL intensity of RL2 band increases as the temperature is increased from 50 K to 100 K. This result was previously reported in Ref. 21 where the PL intensity of the RL2 band increased in the same temperature range. This behavior of PL in the temperature range from 10 K to 60 K was explained by the fact that the lifetime of RL2 band decreased by two orders of magnitude in this temperature range.²¹

The dependence of PL peak intensity on inverse temperature for the RL2 and GL2 bands is shown in Fig. 4.10. At low temperatures, the PL intensity remains unchanged for both these bands. With increasing temperature, at $T > 100$ K, the intensity of the RL2 and GL2 bands starts decreasing exponentially (a linear slope in the Arrhenius plot which is the dependence of the logarithm of PL intensity on inverse

temperature). This quenching of PL reveals the activation energy in the range of 90-120 meV. This is very similar to the results reported for the RL2 and GL2 bands in literature.

4.3.4 Comparison of PL from Ga face and N face for sample 857.14 at 15 K

Figure 4.11 shows two PL spectra: one for Ga-face (CMP-treated) and another for N-face (MP-treated) from as-received semi-insulating bulk GaN (sample 857-14) at 15 K and excitation intensity of 0.3 W/cm^2 . The PL intensity from Ga-face is much higher than that from N-face which means that CMP treatment results in much higher PL intensity than the MP treatment. We assume that the low intensity of the MP-treated N-face is due to the defects at the surface or near the surface.

4.3.5 The effect of sapphire window on PL spectrum from MP surface

Figure 4.12 shows the effect of sapphire window on PL spectrum from N-face which was polished with MP. The measurement first was done by placing a sapphire window on top of the sample to press it harder to the copper holder in order to provide good thermal contact. With this sapphire window, the PL spectrum has a contribution from the window itself because the PL intensity from GaN is extremely low. However, after we removed the sapphire window (by replacing it with a copper washer that presses a sample but allows illuminating the sample and collecting the PL signal) the PL spectrum changed as shown in Fig. 4.12. We can see that the contribution of PL signal from the sapphire window is removed, and the RL2 and GL2 bands can be resolved much better.

4.3.6 PL from pits on Ga-face

The Ga-face of the semi-insulating GaN (sample 857-14, CMP-treated surface) has few pits as shown in Fig. 3.4 and as was mentioned in Section 3.2. We selected two characteristic regions: A and B as shown in Fig. 3.5 where A indicates the pits and B is related to the background area free of the pits. The measurements of PL spectra for this face were done in different regions of the surface of Ga-face and the results are summarized in Figs. 4.13 and 4.14.

First, the PL was measured when the unfocused laser beam illuminated the area with diameter 4 mm which included few small pits (A) and the background (B). Then, the laser beam was directed to one large pit (A) with small contribution from the background area (B). In this experiment, the beam size was decreased to about 1 mm by placing a diaphragm on the way of the laser beam. Next, the PL was collected from the background, free of the pits, which means just in (B). The size of the laser beam was 4 mm again. These three PL scans are shown in Fig. 4.13.

For the first measurement step, when the PL was collected from large area including pits, the PL spectrum consists of intense exciton peak (at about 3.46 eV), the blue luminescence (BL) band with maximum at about 2.95 eV, and the YL band with a maximum at about 2.2 eV. For the next area, when the unfocused laser beam was directed at one large pit and included some background area, the PL spectrum is similar to the previous one but intensity of the YL band intensity increased much. In the last step, PL spectrum from the background area consists of the BL band which is just like the BL band in the first step, but the exciton peak and the YL band decreased.

Finally, the PL was collected with focused laser beam (about 0.2 mm size) from the pit (A) and from the background (B), and these PL spectra are shown in Fig. 4.14. The PL spectrum from the pit shows that the BL band disappears; however, the intensity of the exciton peak and YL band increased significantly. The relative PL intensity (integrated over the entire spectrum) from the pit is much larger than that from the background.

The PL spectra from different regions of this sample show that the pits have different PL spectrum and PL intensity as compared to the background as shown in Fig. 4.14. The pit area shows the YL band, while the background shows the BL band. The high PL intensity from the pits and very low PL intensity from the background can be explained if we assume that the pits contain a conductive GaN which has a high PL intensity, and the background is insulating which has low PL intensity.

4.4 The effect of dry etching on PL from MP surface (sample 1412-4)

4.4.1 The effect of different etching depths on PL intensity

The MP-treated surface of the bulk GaN substrate (Ga face of sample # 1412-4) was etched with RIE method. The etching process was described in Chapter 3. The PL spectra were measured at 15 K and excitation intensity of 0.3 W/cm^2 from different areas which were etched to different depth. The result of this measurement is shown in Fig. 4.15. We can see that the PL intensity from the MP-treated Ga-face increased after etching the sample, and the PL intensity increases with an increase of the depth of etching. The highest depth of about 700 nm depth has a highest PL intensity among other values of

etching such as 0, 50 and 200 nm. RL band (at about 1.8 eV) and GL band (at about 2.4-2.5 eV) were observed in the PL spectra from the area etched to the highest depth (about 700 nm). On the other hand, the control (not etched) area shows the lowest PL intensity and the RL and GL bands disappear. All these results lead to a conclusion that the quality of the Ga-face subjected to MP polish improves dramatically after etching off of about 1 μm of the defective near-surface region. We assume that defects acting as centers of nonradiative recombination are removed by etching. These defects may be extended (cracks, dislocations) and point (impurities, vacancies, interstitials, complexes).

4.4.2 The effect of excitation intensity on PL for dry-etched bulk GaN

The dependence of PL spectrum on excitation intensity from the quarter which was etched to the depth of 700 nm was measured at low temperature and is shown in Fig. 4.16. In this figure the PL intensity decreases with decreasing excitation intensity and both RL and GL bands are observed at different excitation intensities. The RL band partially saturates with increasing excitation intensity.

Chapter 4 Figures

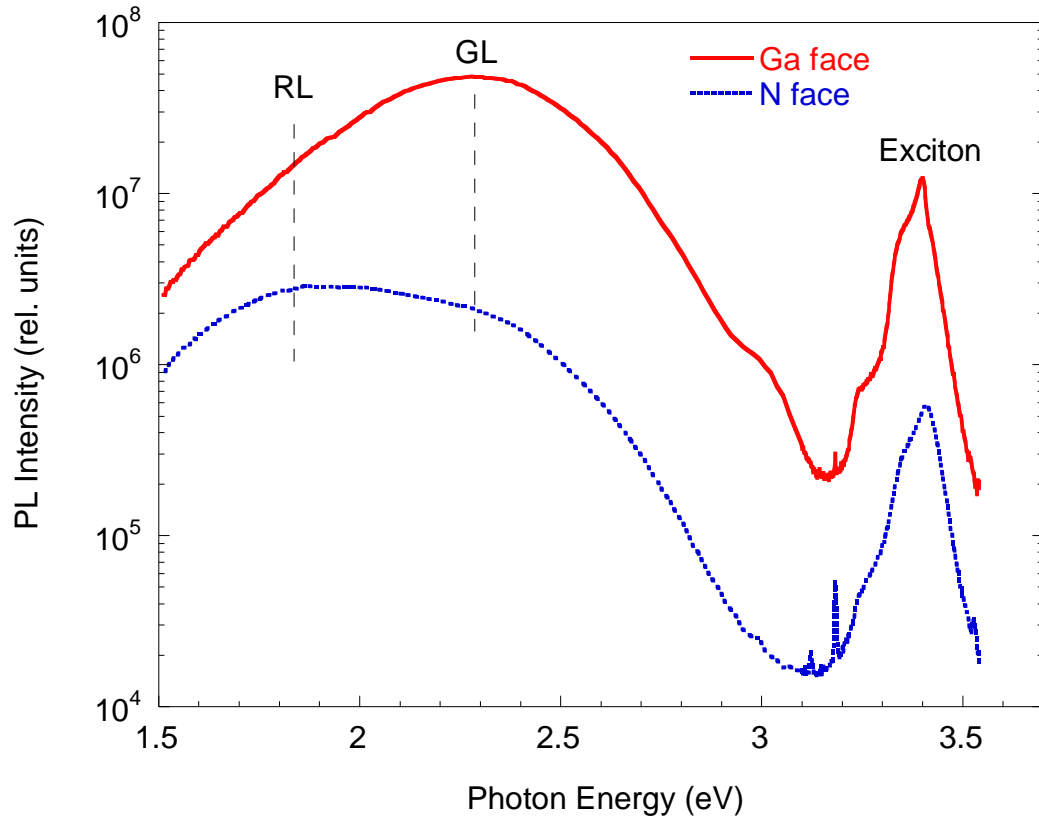


Fig. 4.1: PL spectra from Ga-face (CMP) and N-face (CMP) undoped GaN (sample 1305-3) at room temperature and $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

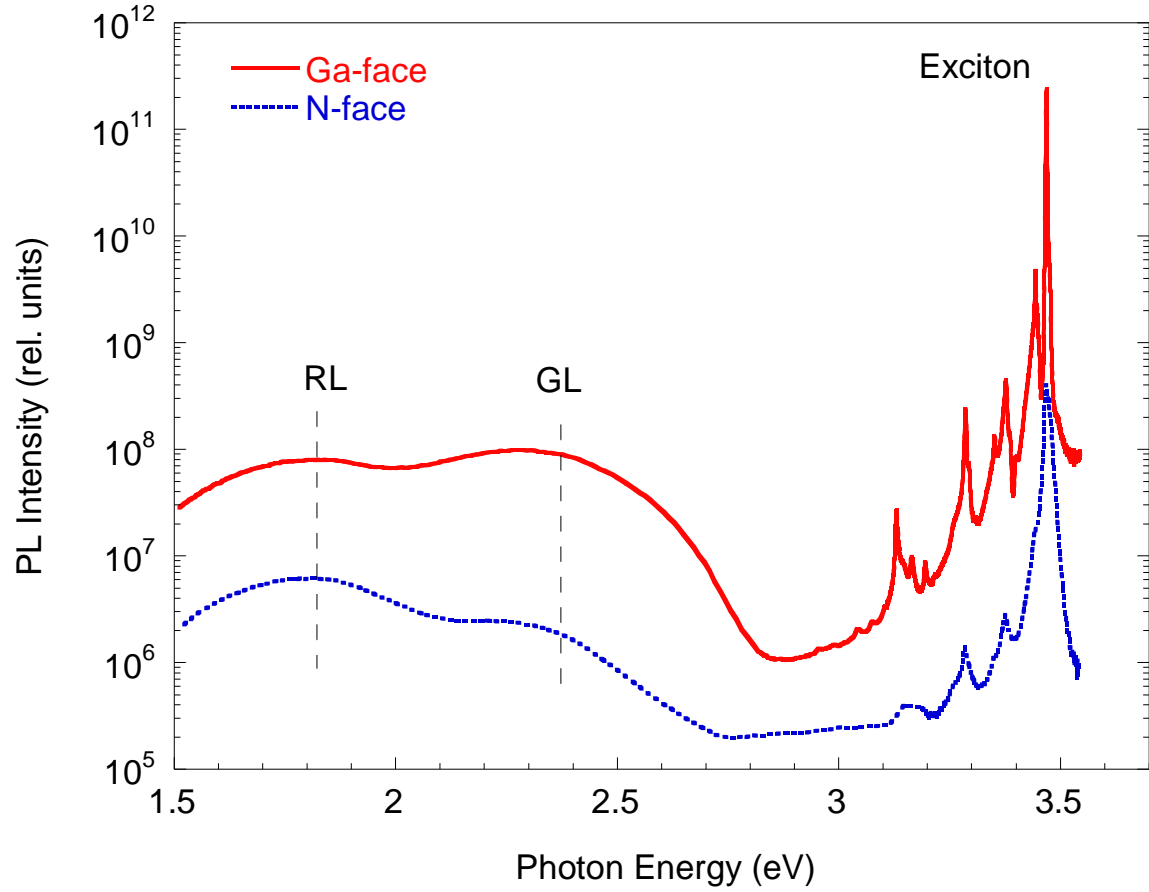


Fig. 4.2: PL spectra from Ga-face (CMP) and N-face (CMP) undoped GaN (sample 1305-3) at low temperature about 15 K and $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

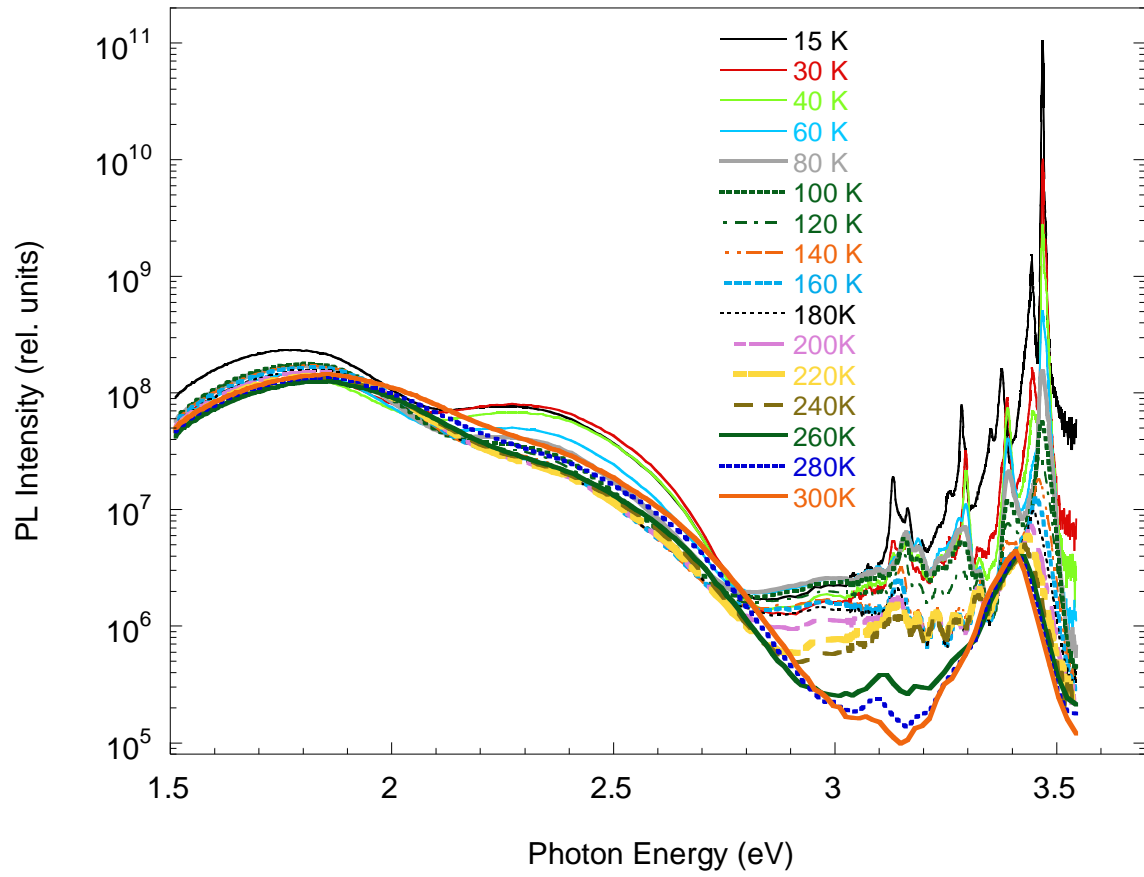


Fig. 4.3: PL spectra from Ga-face (CMP) undoped GaN (sample 1305-3) at different temperatures and $P_{\text{exc}} = 0.0017 \text{ W/cm}^2$

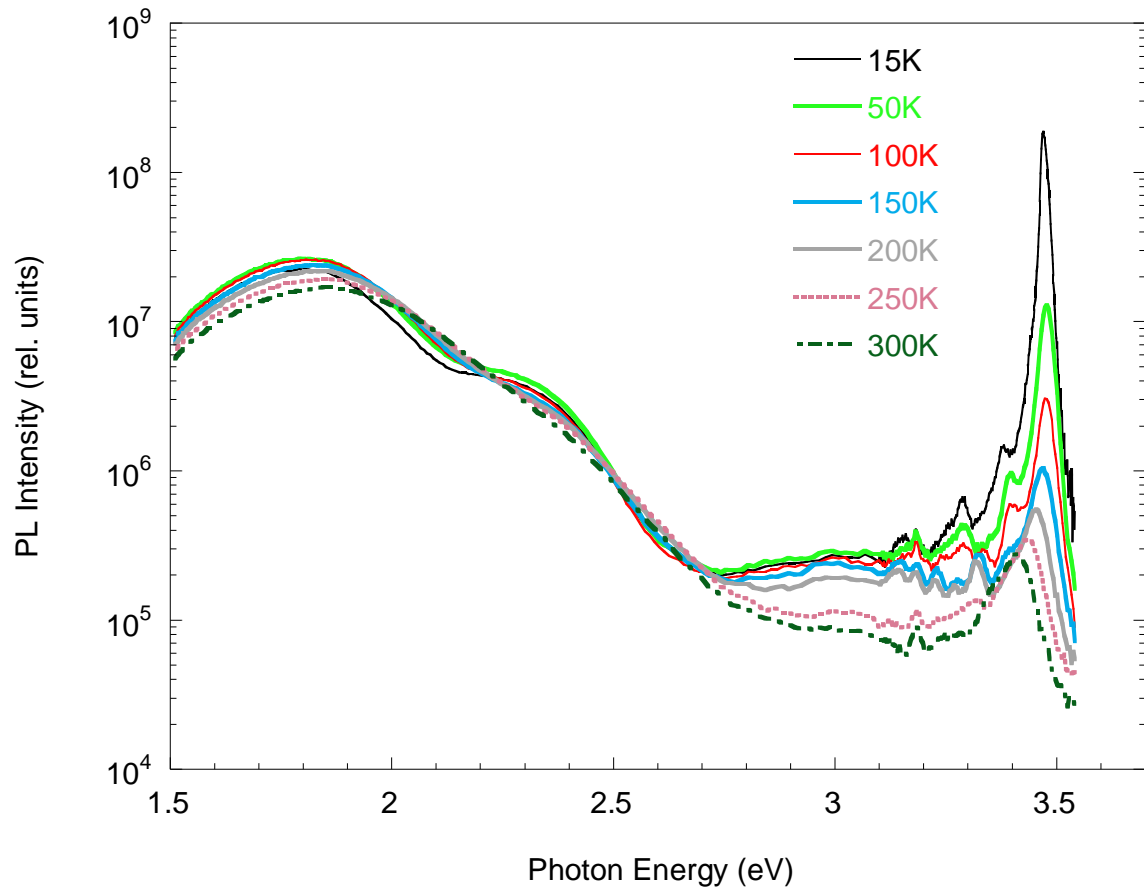


Fig. 4.4: PL spectra from N-face (CMP) undoped GaN (sample 1305-3) at different temperatures and $P_{\text{exc}} = 0.0017 \text{ W/cm}^2$

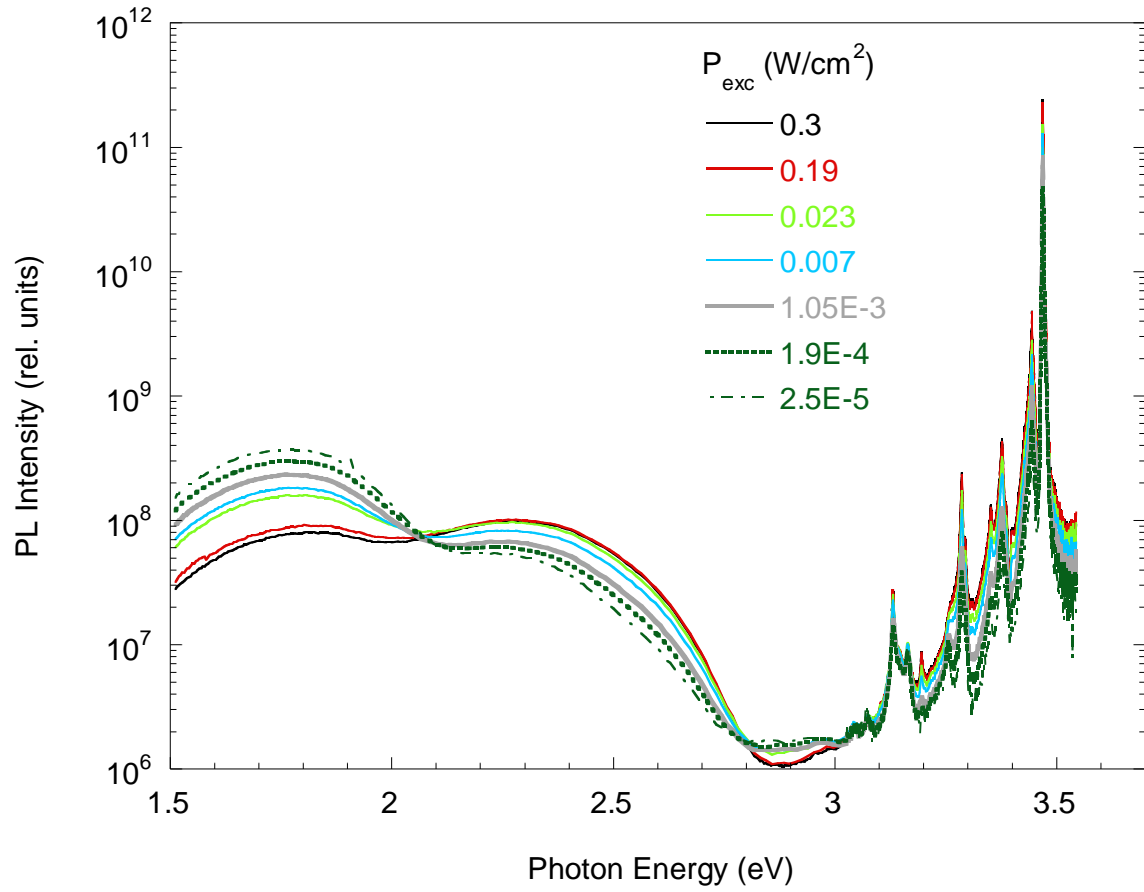


Fig. 4.5: PL spectra at different excitation intensities for Ga-face (CMP) undoped GaN (sample 1305-3) at $T = 15$ K.

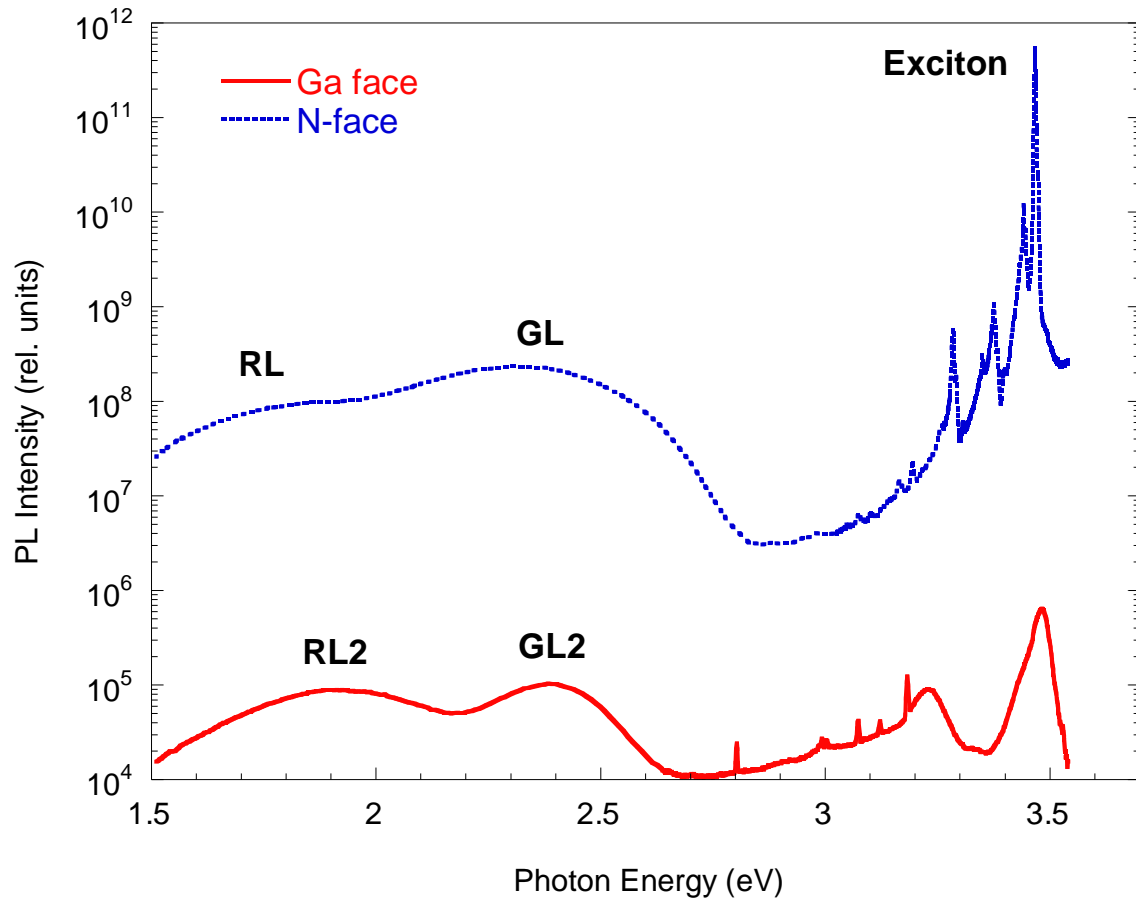


Fig. 4.6: PL spectra from Ga-face (MP) and N-face (CMP) undoped GaN (sample 1412-4) at temperature $T = 15$ K and $P_{\text{exc}} = 0.3$ W/cm²

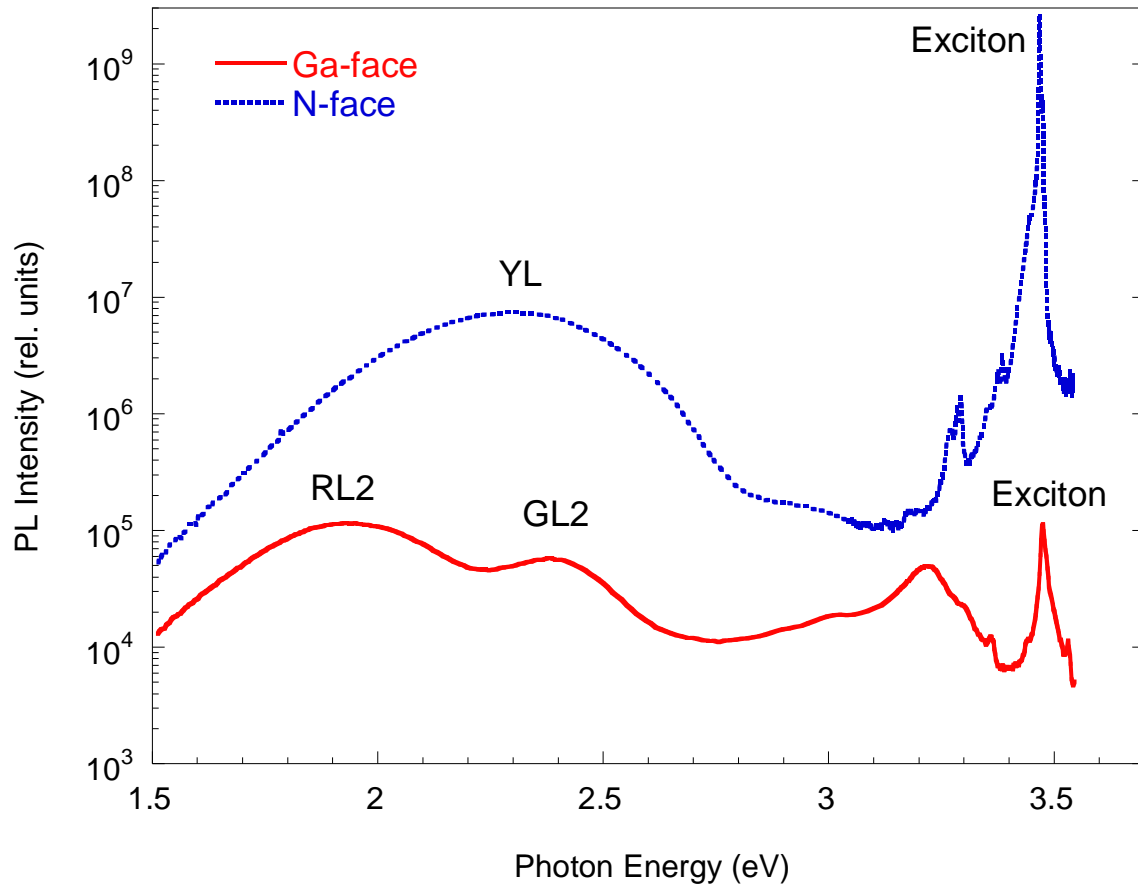


Fig. 4.7: PL spectra from Ga-face (MP) and N-face (CMP) Fe-doped GaN (sample 857-3) at $T = 15$ K and, $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

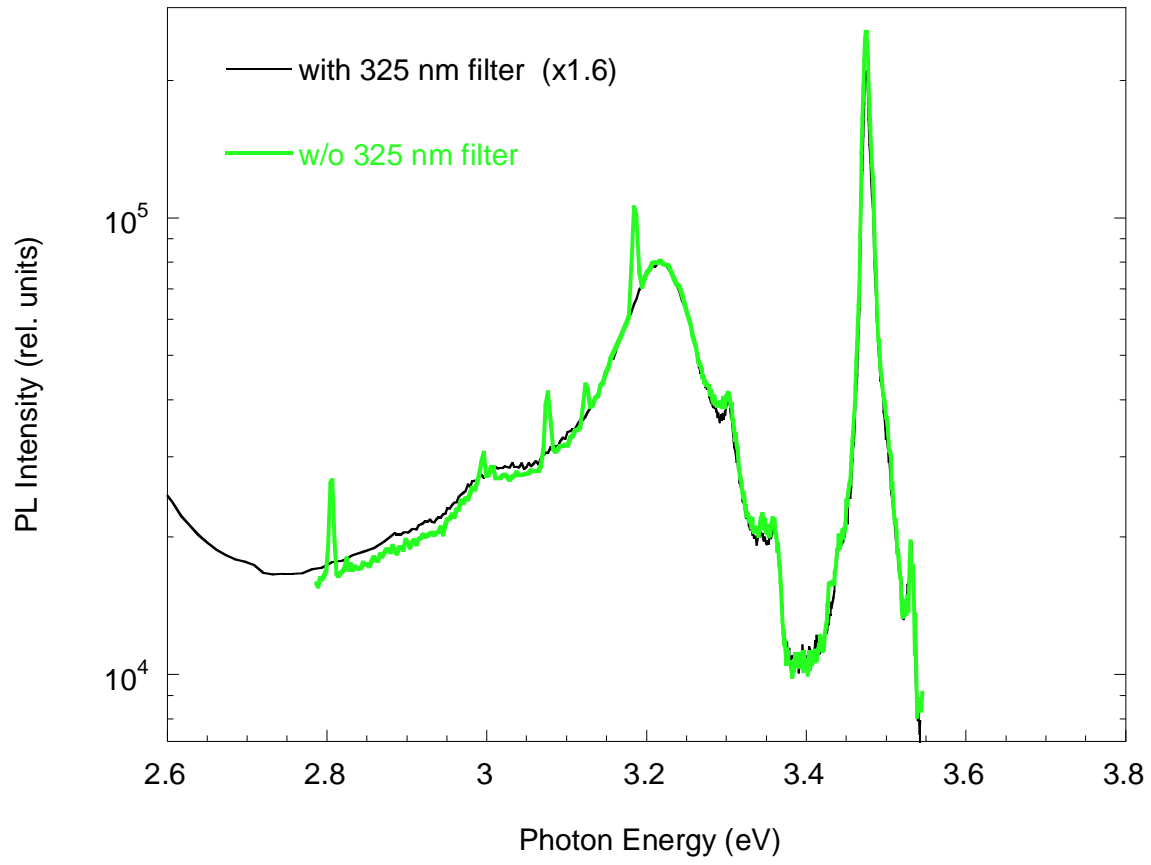
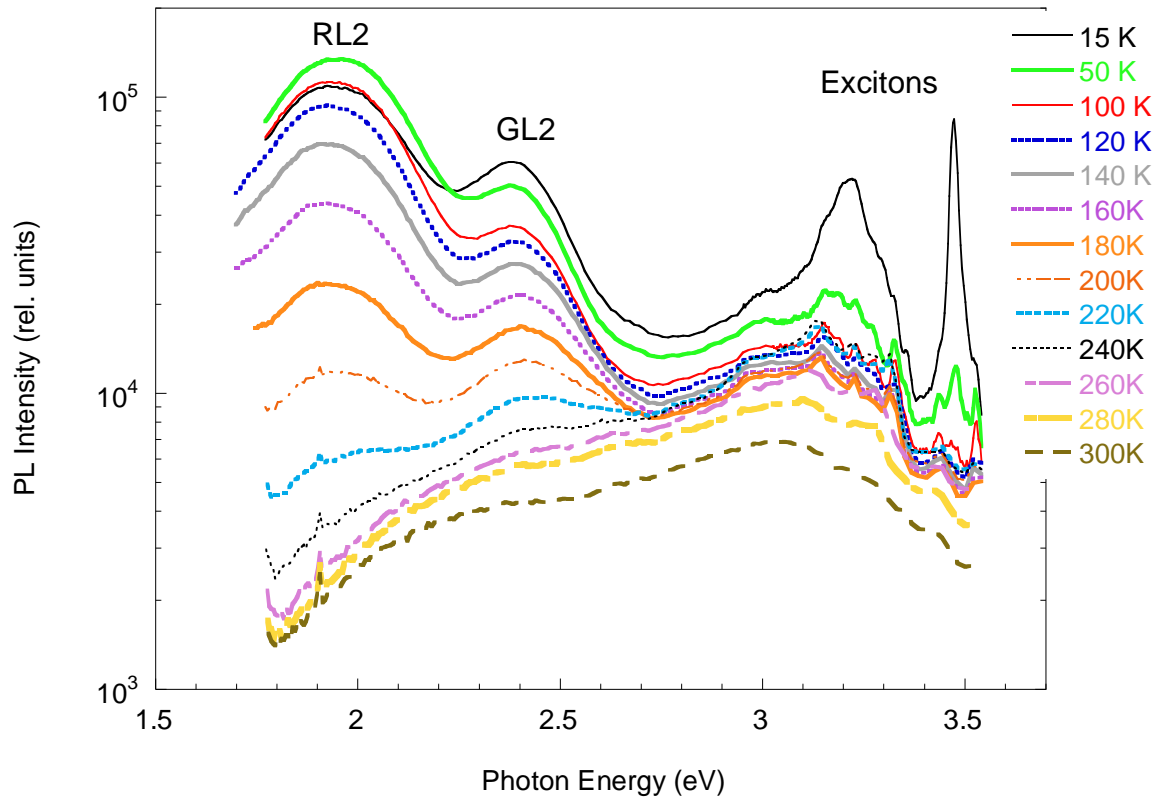


Fig. 4.8: PL spectra from Ga-face (MP) Fe-doped GaN (sample 857-3) with using 325 nm filter and without filter at $T = 15$ K, $P_{\text{exc}} = 0.3$ W/cm²



Fig, 4.9: Temperature dependence of PL spectrum for Ga-face (MP) Fe-doped GaN (sample 857-3) at $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

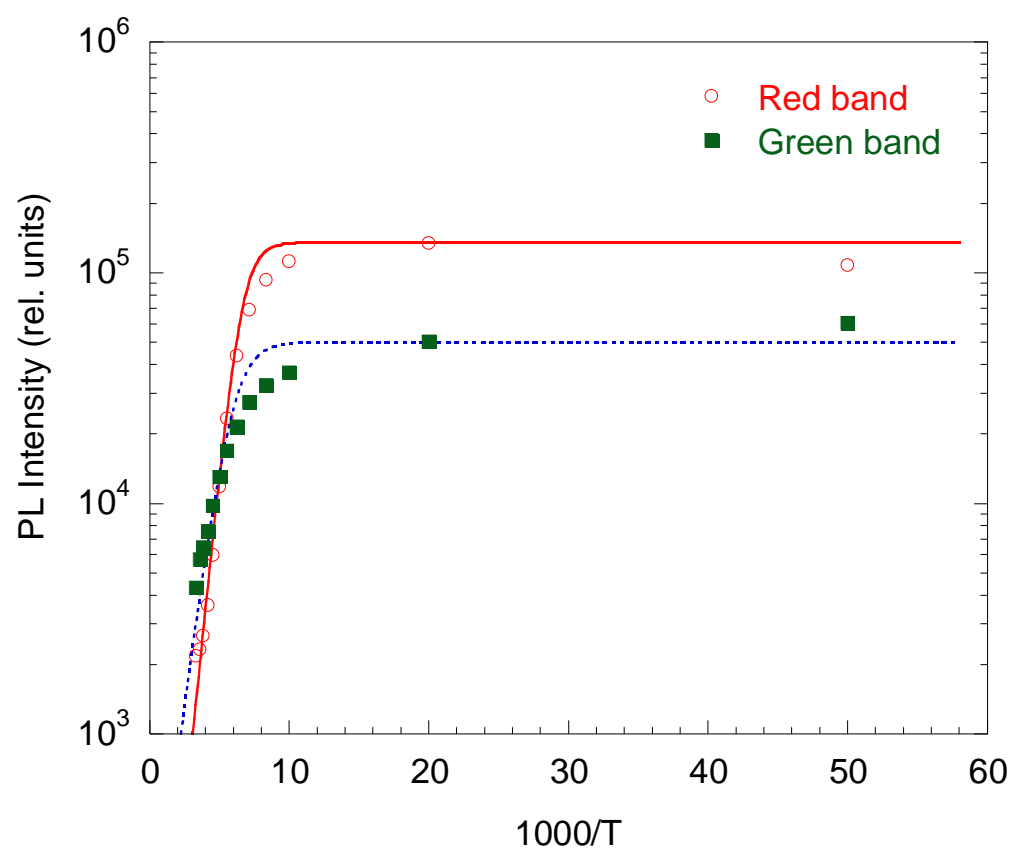


Fig. 4.10: PL intensity as a function of inverse temperature for the RL2 and GL2 bands from Ga-face (MP) Fe-doped GaN (sample 857-3).

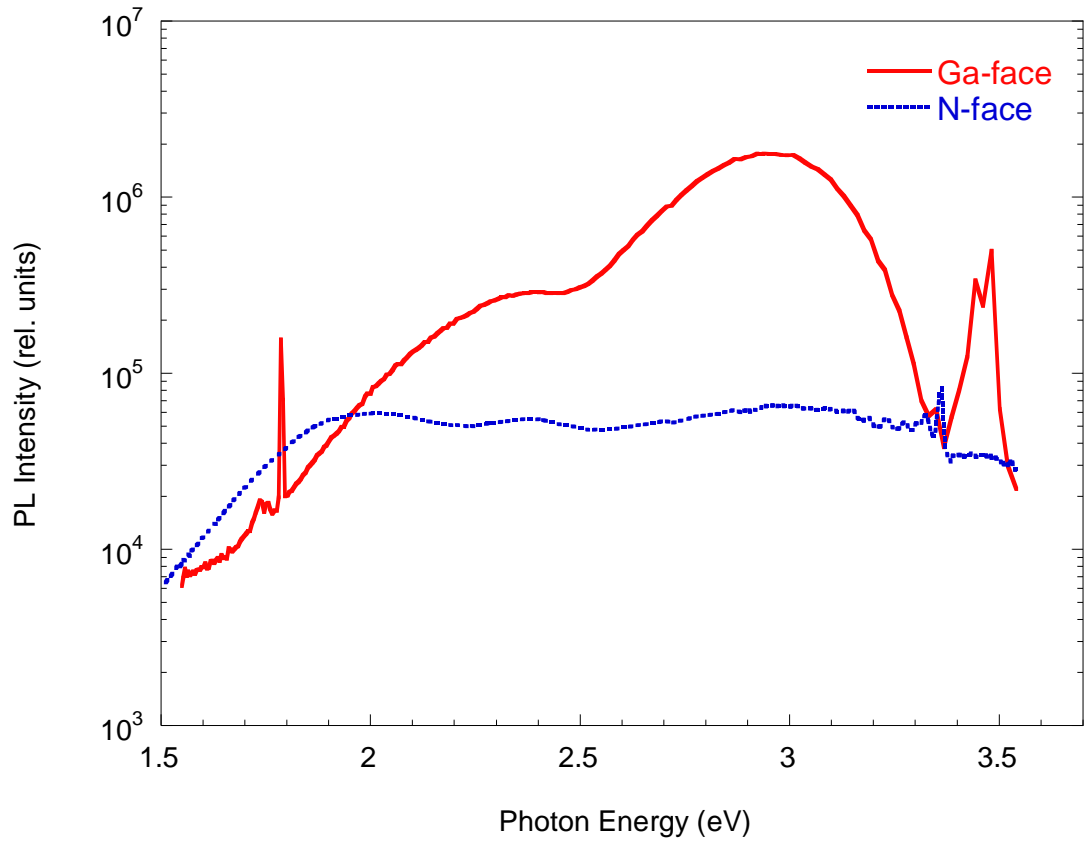


Fig. 4.11: PL spectra from Ga-face (CMP) and N-face (MP) Fe-doped GaN (sample 857-14) at $T = 15$ K, $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

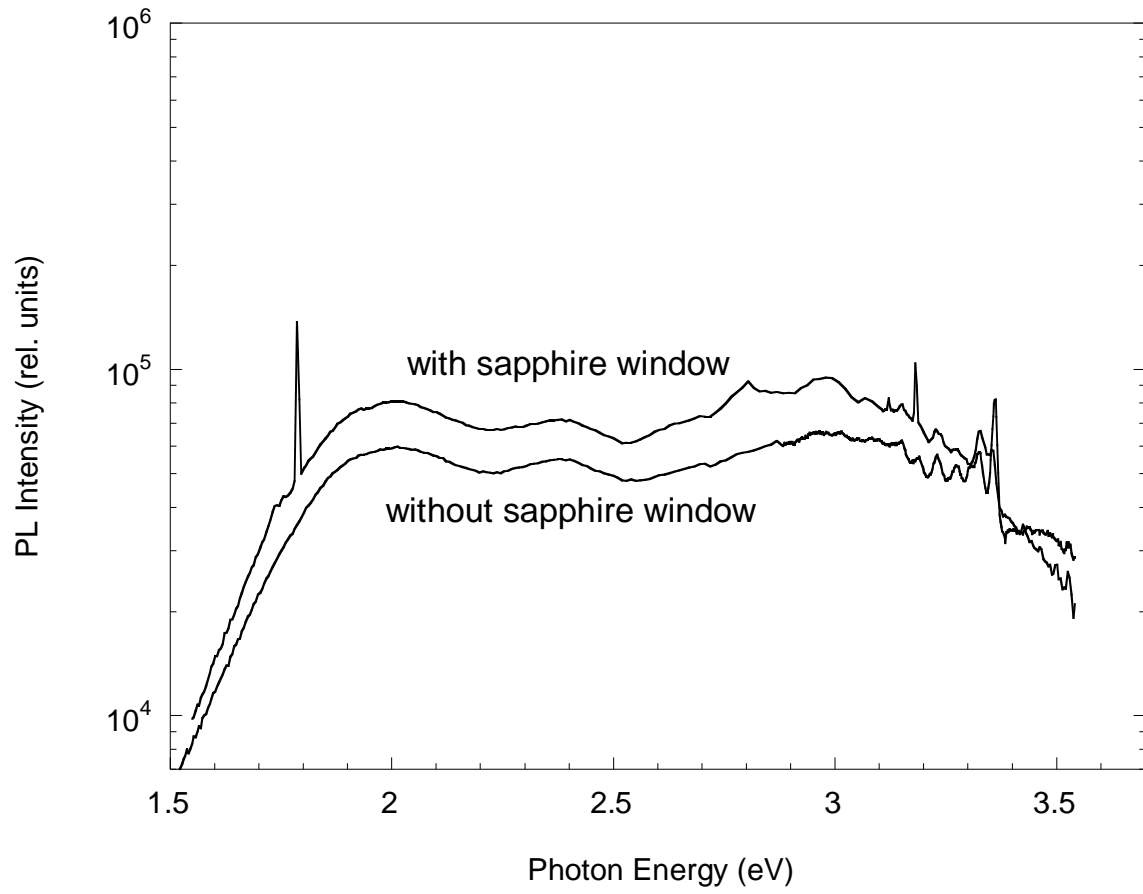


Fig. 4.12: PL spectra from N-face (MP) Fe-doped GaN (sample 857-14) with using sapphire window and without the window at $T = 15$ K, $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

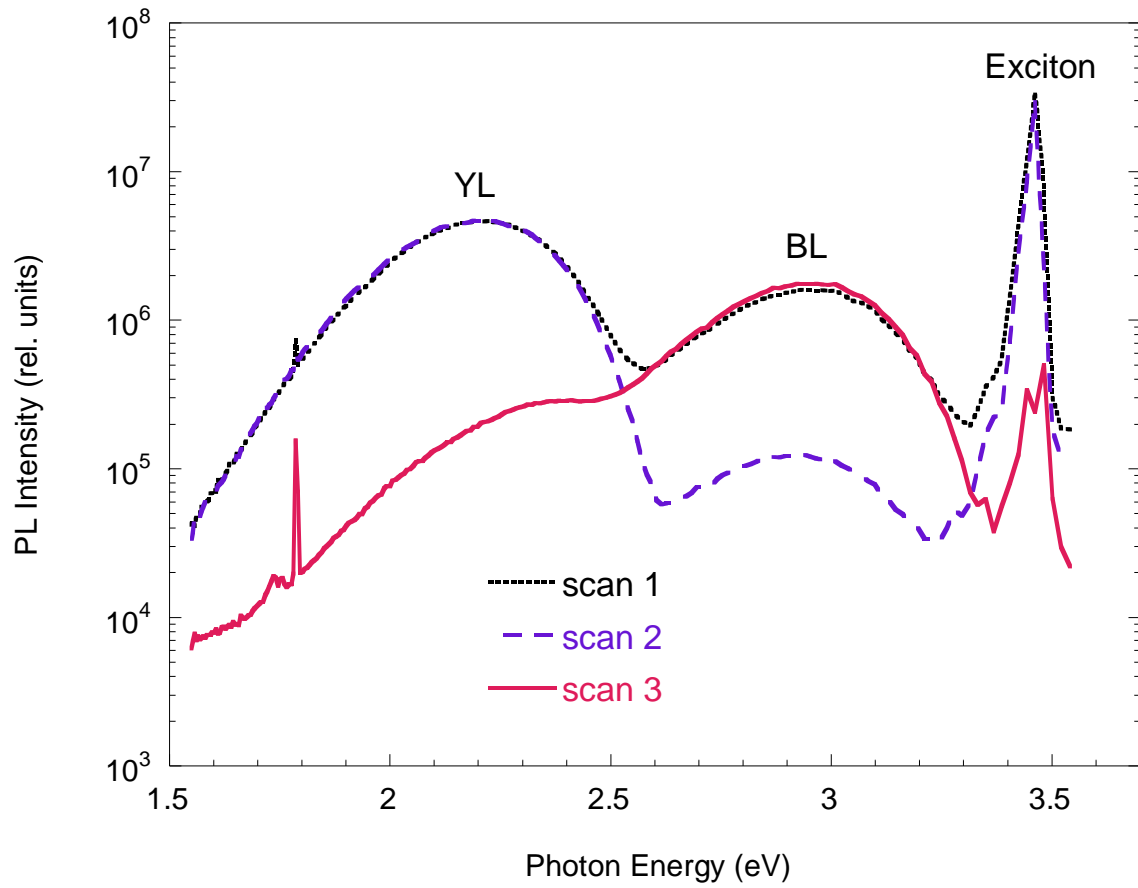


Fig. 4.13: PL spectra from Ga-face (CMP) of Fe-doped GaN (sample 857-14) obtained with unfocused HeCd laser. Three scans correspond to the following measurements: 1) area with small pits (A) and the background (B); 2) area with one large pit (A) and small contribution from the background (B), the beam reduced to the size of 1 mm; 3) area free of pits (just the background (B)) at $T = 15$ K, $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

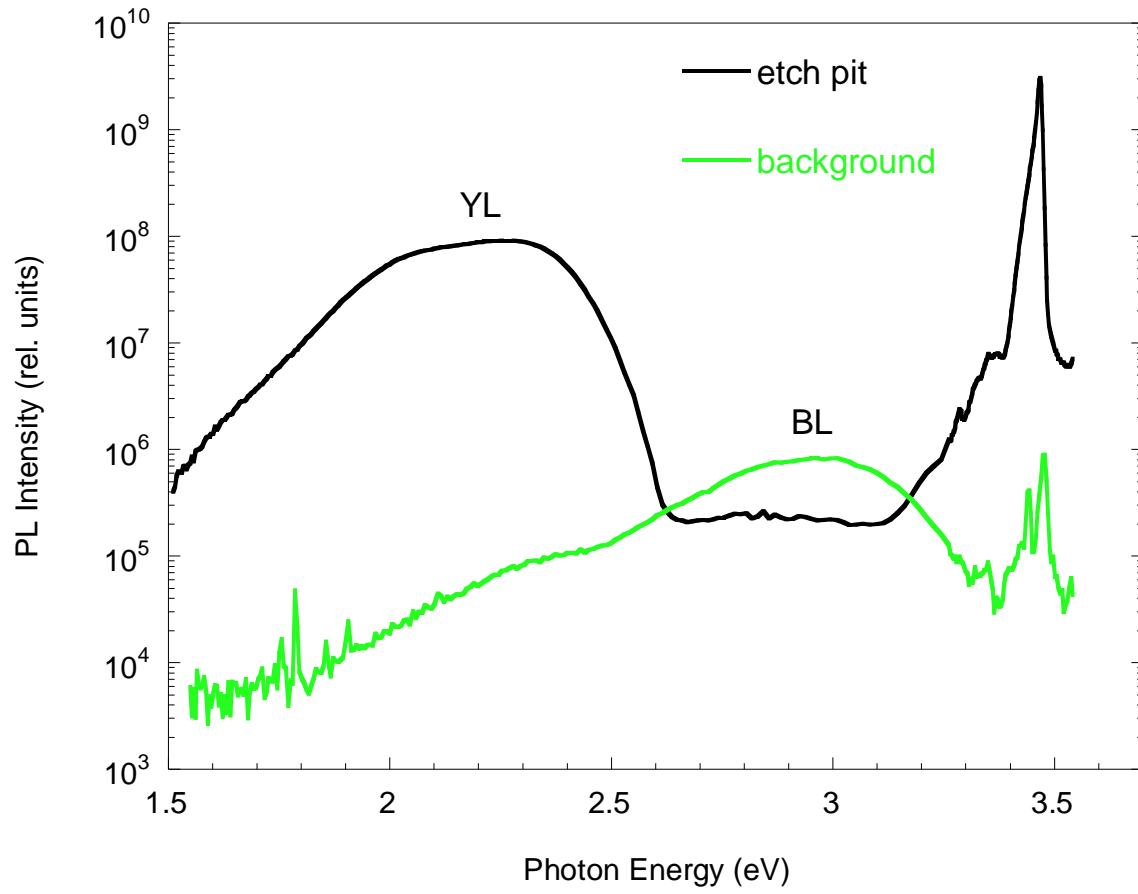


Fig. 4.14: PL spectra taken with a focused HeCd laser from Ga-face (CMP) of Fe-doped GaN (sample 857-14) at temperature of about 15 K and at $P_{\text{exc}} = 0.56 \text{ W/cm}^2$

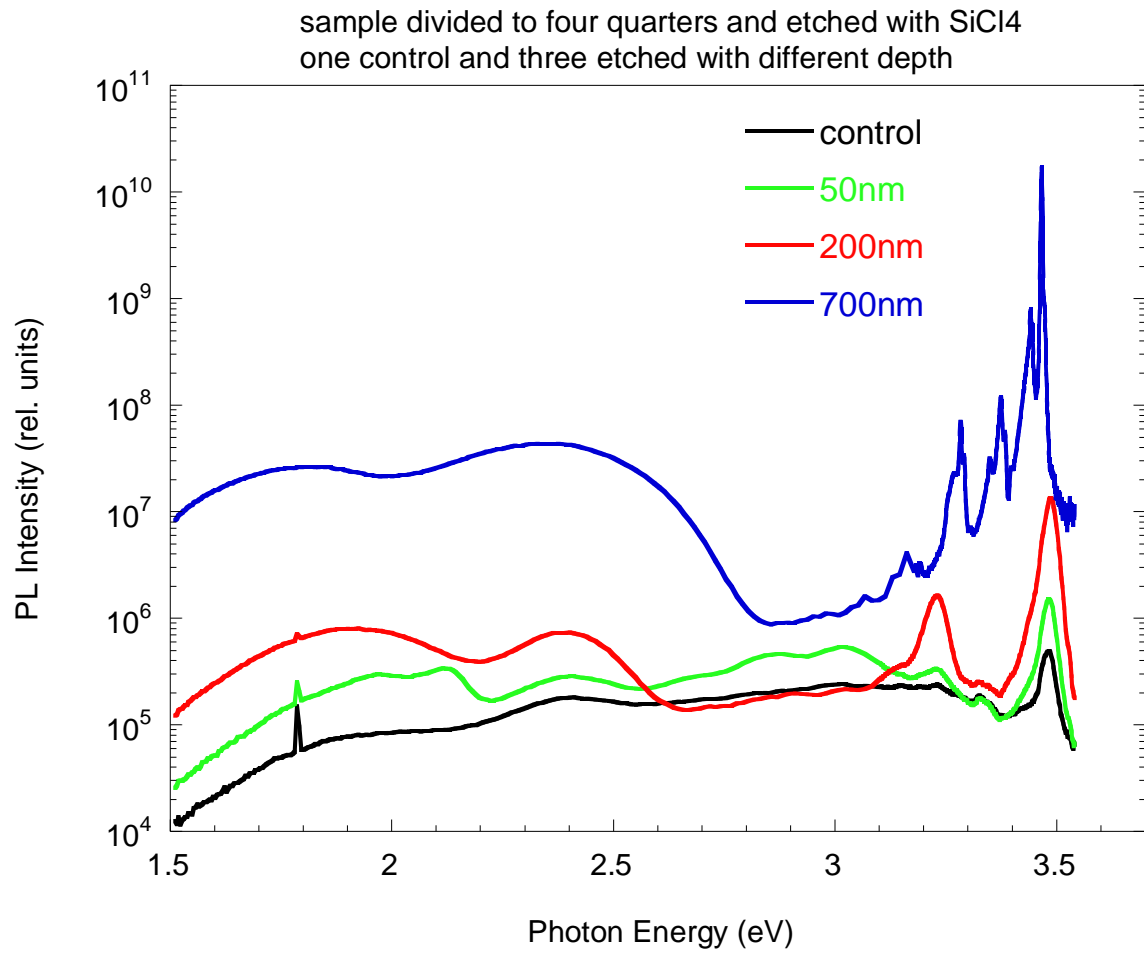


Fig. 4.15: PL spectra from different areas of the Ga-face (MP) undoped GaN (sample 1412-4) etched by RIE to different depths. $T = 15 \text{ K}$, $P_{\text{exc}} = 0.3 \text{ W/cm}^2$

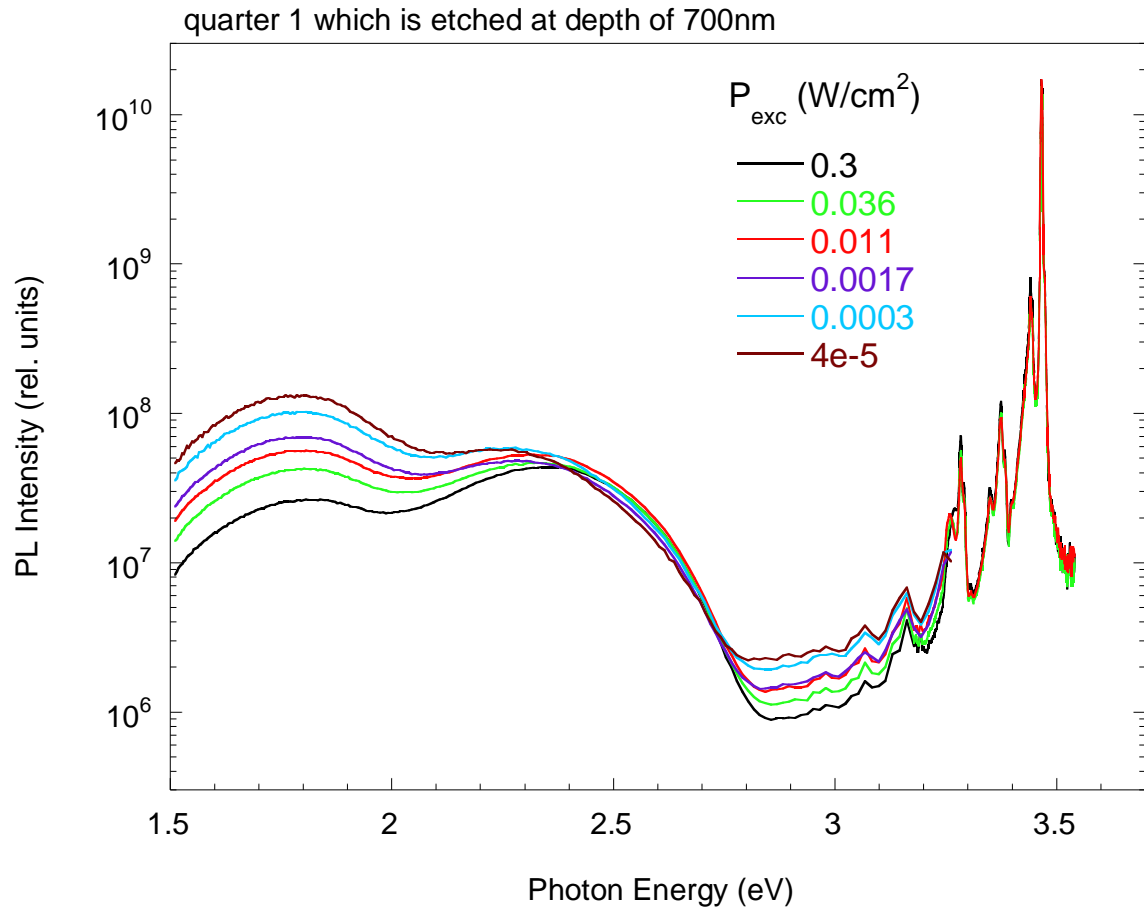


Fig. 4.16: PL spectra (divided on excitation intensity) at different excitation intensities from RIE-etched (700 nm) Ga-face (MP) undoped GaN (sample 1412-4) at $T = 15$ K.

Chapter 5: Summary

Different types of bulk GaN samples (undoped and Fe-doped) grown by HVPE technique at Kyma Technologies have been studied with photoluminescence (PL). Measurements have been performed from surfaces treated with chemical-mechanical polish (CMP) and mechanical polish (MP). In general, we observed that for all the samples, the PL intensity from the CMP-treated surfaces is much higher than that from the MP-treated surfaces due to some defects formed during the process of MP polish.

We observed for undoped high-quality GaN that PL from CMP-treated Ga face is stronger than that from the CMP-treated N face. Further, we observed that the CMP surface of undoped bulk GaN has higher PL intensity than that from CMP surface of Fe-doped samples. PL from the CMP surfaces of undoped bulk GaN samples contains a broad RL band and a broad GL band which are associated with unknown defects. However, PL from the CMP surfaces of Fe-doped GaN samples contained the blue (BL) band. Pits from CMP-surface of Fe-doped sample produced bright yellow (YL) band, and the background of this sample produced only the BL band. We assume that the background is insulating and the pits are n-type which is conductive.

However, MP surfaces for both undoped and Fe-doped bulk GaN samples have very low PL intensities and they all contain relatively narrow red (RL2) and green (GL2) bands which are related to unknown defects but were described in literature. After the MP-treated surface of undoped sample was etched with RIE method, the PL intensity increased by a factor of 1000 due to removal of nonradiative defects from the surface by

etching. We observed that as the depth of etching increases from 50 nm to 700 nm, the PL intensity gradually increases.

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